



Flexible and conductive nanofiber-structured single yarn sensor for smart wearable devices



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ABSTRACT

Electrically conductive fibers or textiles are attractive for their potential applications in wearable devices. The creation of continuously aligned assembly (i.e., bundle or yarn) may enable the realization of supernormal electrical performance of individual nanofibers into macroscale devices. In this study, a conductive polymer based single yarn consisting of core–sheath polyaniline (PANI)/polyacrylonitrile (PAN) nanofibers was fabricated by combining a novel electrospinning method with in-situ solution polymerization process. The as-prepared PANI/PAN uniaxially aligned coaxial nanofiber yarn (UACNY) was utilized to construct an ammonia (NH₃) sensor. We demonstrated that the nanofiber-structured construction in the PANI/PAN UACNY offered a high surface area for the free diffusion of NH₃, and the highly-oriented nanofiber arrangement of the PANI/PAN UACNY facilitated the one-way charge carrier transfer for effectively unidirectional transmission of electrical signals, which both endowed the yarn sensor excellent sensitivity and fast response/recovery upon exposure to NH₃ of 10–2000 ppm at room temperature. Furthermore, the yarn-based sensor presented excellent reproducibility and stability for NH₃ detection. Importantly, the PANI/PAN UACNY sensor possessed robust mechanical strength with flexibility, which could be processed into defined electronic textiles using various textile-forming technologies, i.e., knitting, braiding, and embroidering techniques. The flexible and conductive PANI/PAN UACNY have the potential to be applied for the development of wearable smart textiles, due to their stable structure, handling convenience, excellent mechanical property, as well as high gas sensing performance.

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1. Introduction

Electronic textiles have inspired tremendous interest recently due to their potential applications in wearable electronics and portable devices, such as healthcare detector [1,2], portable power [3–5], work and military uniforms [6–8]. Compared with metals or metal oxides-based electronic components, conductive polymers are suited as the (semi)conductor with intrinsically mechanical

toughness of plastics, and can be Assembled together with other appropriate polymers, which facilitate the manufacturing of flexible fiber-shaped platforms such as bundles, yarns, meshes or other textile constructs [2,9–11].

Conductive polymers-based fibers or textiles gas sensors have generated increasing attention for their required mechanical toughness for easy processing, light weight, low cost, and especially their high sensing performance at room temperature [12,13]. Traditionally, Conductive polymers are coated, polymerized or co-spun with other polymers to generate textile-used yarns, which can be employed as building blocks for generating fiber-shaped textiles architectures [14–16]. Alternatively, conductive polymers are directly synthesized on as-prepared textile constructs for electrically conductive smart textiles application [4,17,18]. However, the fibers utilized in the traditional textile industry usually possess much larger diameters (several microns or above) in comparison with innovative nanofibers. Hence, the microfiber-constructed textiles exhibit relatively low surface-area-to-volume ratio, leading to poor gas sensor performances [19–22].

Abbreviations: PAN, polyacrylonitrile; PANI, polyaniline; UANY, uniaxially aligned nanofiber yarn; UACNY, uniaxially aligned coaxial nanofiber yarn; NH₃, ammonia; ESEM, environmental scanning electron microscopy; FE-SEM, field emission scanning electron microscopy; TEM, transmission electron microscopy; FTIR, fourier transform infrared; NMD, neutral metal disc; NHMR, neutral hollow metal rod; SSA, sulfosalicylic acid dehydrate; APS, ammonium peroxodisulfate; C₂H₅OH, ethanol; CH₃COCH₃, acetone; CH₂Cl₂, dichloromethane.

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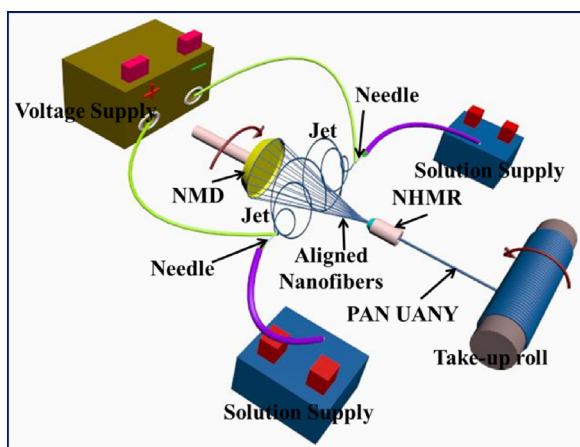


Fig. 1. Schematic illustration of our modified electrospinning setup.

Many nanotechniques have been employed to manufacture sensing materials, taking advantage of their super-high surface-area-to-volume ratio of nanostructured materials [23–27]. Electrospinning has been recognized as an efficient and versatile technique to manufacture nano-sized fibers with diameters in the range of 50–1000 nm [28–31]. Conductive polymers and their blends with other polymers have been electrospun into nanofibers for gas sensor application recently. However, these conductive polymer-based nanofibers were collected into uncontrolled and randomly packed nonwoven mats, resulting in relatively inferior mechanical properties [32–37]. The obtained conductive polymer-based nanofiber mats are limited as an ideal manufacturing unit to further tailor into different fabric architectures for the application in smart textiles. To overcome the aforementioned concerns, the fabrication of conductive polymers-based nanofiber yarns by modified electrospinning technique would be of substantial interest to incorporate the excellent electrical-chemical characteristics of individual nanofibers with supernormal textile processibility. There have been no reports to date on conductive polymer-based nanofiber yarn gas sensors. Herein, we report a new processing method for effectively fabricating conductive polymers-based uniaxially aligned coaxial nanofiber yarns (UACNY). Polyacrylonitrile (PAN) core-layered nanofibers were electrospun from a novel electrospinning system and were employed as templates to generate uniform sheaths of polyaniline (PANI) by in-situ solution polymerization process. To pursue their potential gas sensing applications, the electrical responses of PANI/PAN UACNY towards ammonia (NH_3) gas were measured at room temperature. Moreover, PANI/PAN UACNY were explored to manufacture different textile architectures by employing various textile-forming techniques, demonstrating the versatility and feasibility of as-fabricated PANI/PAN UACNY for smart textile applications.

2. Experimental details

2.1. Fabrication of PANI/PAN UACNY

Two steps were employed to prepare PANI/PAN UACNY. First, PAN (molecular weight of 75,000, Shanghai Chemical Fibers Institute) was dissolved thoroughly in *N,N*-Dimethylformamide (DMF) with a concentration of 10% (w/w) as the electrospinning solution. A novel electrospinning device designed by our group was used to continuously manufacture PAN uniaxially aligned nanofiber yarns (UANY) [38,39]. Fig. 1 shows the schematic of the novel electrospinning setup. Here, the distance between two needles, distance between neutral metal disc (NMD) and neutral hollow metal rod (NHMR), applied voltages of two needles, solution flow rate,

rotation speed of NMD and linear velocity of take-up roll were maintained at 20 cm, 7 cm, ± 10 kV and 0.8 ml/h, 250 r/min and 2 m/min, respectively.

PANI layers was subsequently synthesized on the surface of PAN nanofibers of as-electrospun PAN UANY through an in-situ chemical oxidative polymerization process, in order to generate core-sheath PANI/PAN nanofibers as shown in Fig. 2. The reaction solution was prepared as followed: Firstly, 2.5 mmol aniline monomers and 2.5 mmol sulfosalicylic acid dehydrate (SSA) were dissolved thoroughly in 50 ml deionized water named solution A. Secondly, 2.5 mmol ammonium peroxodisulfate (APS) was added and stirred homogeneously in 50 ml deionized water named solution B. Thirdly, the solution A and solution B were mixed together and the PAN UANY were fully immersed in the mixed solution and kept steady at 0 °C for 12 h. Finally, the dark green single yarns composed with coaxial PANI/PAN nanofibers were removed out and washed by deionized water and ethanol for several times and dried in a vacuum at room temperature overnight.

2.2. Materials characterization

The morphology of the obtained PANI/PAN UACNY was examined by environmental scanning electron microscopy (ESEM, QUANTA250, FEI) and field emission scanning electron microscopy (FE-SEM, S-4800, HITACHI). Transmission electron microscopy (TEM, JEM-2100, JEOL) was used to observe the coaxial structure of the PANI/PAN nanofibers in UACNY. Fourier transform infrared (FTIR) spectrometer (NEXUS-670, Nicolet) in attenuated total reflectance (ATR) mode was employed to investigate the functional groups of the PANI/PAN UACNY. Mechanical characterization of all samples was performed by a XQ-2 fiber strength tester. For each sample, the gauge length, crosshead speed and test volume were respectively set as 10 mm, 10 mm/min and 20 times.

2.3. Ammonia sensing measurement

The PANI/PAN UACNY with the length of 10 mm was transferred to the surface of a typical interdigitated electrode ($13.4 \text{ mm} \times 7 \text{ mm}$) to construct a gas sensor. Mass flow controllers were used to control the concentrations of the test gas. Dry air was used as the dilution, carrier and purge gas to avoid influence of humidity contained in air. The gas sensing characteristics of the PANI/PAN UACNY sensor were investigated by recording their electrical responses when exposed alternately to the ammonia gas and dry air using the CGS-1TP intelligent test system (Beijing Elite Tech Co.Ltd., China) connected to a computer. The test chamber with 18 l volume was used and the NH_3 gas with the concentrations of 10–2000 ppm was tested. The sensor response was determined as R_g/R_a ratio, where R_g and R_a were the resistances of sensor in air-gas mixture and air ambience. The time taken by sensor resistance to change from R_a to $R_a + 90\%$ ($R_g - R_a$) was defined as the response time in the case of NH_3 adsorption, while the time taken by sensor resistance to change from R_g to $R_g - 90\%$ ($R_g - R_a$) was defined as the recovery time in the case of NH_3 desorption. All sensing measurements were performed at room temperature (25 °C).

3. Results and discussion

3.1. Morphology and structure of the PANI/PAN UACNY

Fig. 3A shows the appearance of PAN UANY package produced from a novel electrospinning method, which was manufactured continuously for about 4 h. Then electrospun PAN UANY were employed as a template to generate PANI/PAN UACNY, and the morphology of PANI/PAN UACNY produced after the in-situ solution polymerization process was shown in Fig. 3B. The white PAN

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